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(54) Title: ORGANIC CETANE IMPROVER

(57) Abstract: Embodiments of the invention described herein increase the amount of cetane in fuel. Cetane improvers comprising  $\beta$ -carotene, which was prepared in an inert atmosphere, as well as, methods of preparing such compositions are described. A preferred composition is a No. 2 diesel fuel comprising a cetane improver, which comprises a  $\beta$ -carotene that was prepared in an inert atmosphere.

**ORGANIC CETANE IMPROVER****FIELD OF THE INVENTION**

The present invention relates generally to a composition and method for increasing the amount of cetane in fuel. More specifically, it was discovered that the amount of cetane in fuel can be increased by mixing a fuel additive  
5 comprising  $\beta$ -carotene that was prepared in an inert atmosphere.

**BACKGROUND OF THE INVENTION**

The interest in improving fuel efficiency has become paramount as our natural resources dwindle and the cost of fuel continues to rise. Fuel efficiency can be improved by adding a fuel additive. Several existing fuel additives are known to increase fuel efficiency, for example, U.S. Patent Nos. 4,274,835, 5,826,369, and 6,193,766 describe  
10 fuel additives that improve combustion. Despite the successes of these inventions, there still remains a need for fuel additives that improve combustion.

**BRIEF SUMMARY OF THE INVENTION**

Embodiments of the invention described herein concern fuel additives that increase the amount of cetane in fuel and methods of use thereof. In one embodiment, for example, a method of improving the amount of cetane in a  
15 fuel comprises the step of adding a  $\beta$ -carotene that was dissolved in an inert atmosphere to said fuel. In another embodiment, a cetane improver is made by providing  $\beta$ -carotene that was dissolved in an inert atmosphere, providing an alkyl nitrate, and mixing the  $\beta$ -carotene with the alkyl nitrate. In aspects of this later embodiment, the alkyl nitrate is 2-ethylhexyl nitrate or the inert atmosphere is nitrogen. Additionally, this later method of making a cetane improver can further comprise the step of mixing the  $\beta$ -carotene with toluene prior to mixing the  $\beta$ -carotene with the alkyl  
20 nitrate.

Compositions of the invention can include, for example, a cetane improver made by one of the methods described above or a cetane improver comprising a non-oxygenated  $\beta$ -carotene. These cetane improver embodiments can also comprise an alkyl nitrate and/or a toluene. Additionally, in some compositions, the alkyl nitrate is 2-ethylhexyl nitrate. A preferred embodiment of the invention is a No. 2 diesel fuel comprising one of the cetane improvers  
25 described above.

**DESCRIPTION OF THE INVENTION**

The invention described herein concerns a composition and method for increasing the amount of cetane in fuel. In one embodiment the cetane improver comprises  $\beta$ -carotene that was prepared under an inert atmosphere. Unexpectedly, it was discovered that  $\beta$ -carotene, which was dissolved in an inert atmosphere, raised the level of  
30 cetane in No. 2 diesel fuel more effectively and maintained the raised cetane level longer than  $\beta$ -carotene prepared by conventional methods. In preferred embodiments, a cetane improver is prepared by mixing  $\beta$ -carotene that was dissolved in an inert atmosphere with a toluene carrier, and an alkyl nitrate (e.g., 2-ethylhexyl nitrate). The preferred cetane improver prepared by the methods described herein increased the level of cetane in No. 2 diesel fuel in a synergistic fashion.

In a preferred form, the cetane improver can be formulated by the following method. Under an inert atmosphere, (e.g., nitrogen, helium, or argon) four grams of  $\beta$ -carotene (1.6 million International units of vitamin A activity per gram) are dissolved in 3.785 liters of liquid hydrocarbon carrier toluene with heating and stirring.  $\beta$ -carotene dissolved or otherwise prepared under an inert atmosphere is referred to as "non-oxygenated  $\beta$ -carotene".

5 The mixture of non-oxygenated  $\beta$ -carotene and toluene is referred to as a "B/C-toluene solution". Approximately, 946 milliliters of the B/C-toluene solution is removed. Next, approximately 946 milliliters of a 100% solution of 2-ethylhexyl nitrate (also referred to as "2-EHN") is added to the 2.839 liters of B/C-toluene solution so as to obtain a total volume of 3.785 liters. That is, approximately 25% of the starting volume of B/C-toluene is removed and replaced by an equal volume of 2-ethylhexyl nitrate.

10 It should be understood that pure 2-EHN is desired but that variations in alkyl nitrates and in grade are also suitable. Further, one of skill will appreciate that other alkyl nitrates are equivalent to 2-EHN and can be substituted accordingly. Desirably, many different formulations of cetane improver are made, each having a different alkyl nitrate or more than one alkyl nitrate and/or proportions thereof relative to the  $\beta$ -carotene, which was dissolved under an inert atmosphere, and these formulations are evaluated for the ability to raise cetane levels in No. 2 diesel fuel according to the methods described below. In the embodiment described above, it is desirable to add the ingredients in the order described above. However, in other embodiments, variations in the order of addition can be made.

The B/C-toluene-2-EHN solution is one embodiment of a "concentrated cetane improver," also referred to as "OR-CT." To improve the cetane level in No. 2 diesel fuel, approximately 0.1ml - 35ml of the concentrated cetane improver is added per one gallon of No. 2 diesel fuel. Preferably, the amount of concentrated cetane improver added to a gallon of No. 2 diesel fuel is, in the range from about 0.3 ml to about 30ml, more desirably, from about 0.5ml to about 25ml, still more preferably, from about 0.75ml to about 20ml, even more preferably, from about 1ml to about 15ml, and most preferably, from about 2ml to about 12ml. The *Examples* described below provide the results of tests performed according to the well accepted ASTM D-613 procedure on baseline fuels of various quality as measured by initial cetane levels. This data verifies that the cetane improver described herein synergistically improves the level of cetane in No. 2 diesel fuel.

#### EXAMPLE 1

FORMULATION	CETANE LEVEL
Baseline fuel No. 2 Diesel	40.5
No. 2 diesel with 1057 <sup>1</sup> ppm 2-EHN <sup>8</sup> only	44.98
No. 2 diesel with 1057 <sup>1</sup> ppm OR-CT <sup>3</sup> only	43.04
No. 2 diesel with 528.5 <sup>2</sup> ppm 2-EHN <sup>8</sup> + 528.5 <sup>2</sup> ppm OR-CT <sup>3</sup> mixed	45.39(+0.41)

## EXAMPLE 2

<u>FORMULATION</u>	<u>CETANE LEVEL</u>
Baseline fuel No. 2 Diesel	46.8
No. 2 diesel fuel with 1057 <sup>1</sup> ppm 2-EHN <sup>6</sup> only	52.75
No. 2 diesel fuel with 1057 <sup>1</sup> ppm OR-CT <sup>3</sup> only	50.81
No. 2 diesel fuel with 528.5 <sup>2</sup> ppm 2-EHN <sup>6</sup> + 528.5 <sup>2</sup> ppm OR-CT <sup>3</sup> mixed	54.02(1.27)

## EXAMPLE 3

<u>FORMULATION</u>	<u>CETANE LEVEL</u>
Baseline fuel No. 2 diesel	48.79
No. 2 diesel fuel with 1057 <sup>1</sup> ppm 2-EHN <sup>6</sup> only	53.18
No. 2 diesel fuel with 1057 <sup>1</sup> ppm OR-CT <sup>3</sup> only	51.13
No. 2 diesel fuel with 528.5 <sup>2</sup> ppm 2-EHN <sup>6</sup> + 528.5 <sup>2</sup> ppm OR-CT <sup>3</sup> mixed	54.52(+1.34)

## EXAMPLE 4

<u>FORMULATION</u>	<u>CETANE LEVEL</u>
Baseline fuel No. 2 diesel	40.5
No. 2 diesel fuel with 300 <sup>4</sup> ppm 2-EHN <sup>6</sup> only	43.02
No. 2 diesel fuel with 300 <sup>4</sup> ppm OR-CT <sup>3</sup> only	41.48
No. 2 diesel fuel with 150 <sup>5</sup> ppm 2-EHN <sup>6</sup> + 150 <sup>3</sup> ppm OR-CT <sup>3</sup> mixed	43.34(+0.32)

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<sup>1</sup> = 4 milliliters per gallon

<sup>2</sup> = 2 milliliters per gallon

<sup>3</sup> = 1 X 10<sup>6</sup> IU  $\beta$ -carotene

<sup>4</sup> = 1.14 milliliters per gallon

<sup>5</sup> = 0.57 milliliters per gallon

<sup>6</sup> = 2-ethylhexyl nitrate

Although the invention has been described with reference to embodiments and examples, it should be understood that various modifications can be made without departing from the spirit of the invention. Accordingly, the invention is limited only by the following claims. All references cited herein are hereby expressly incorporated by reference in their entireties.

WHAT IS CLAIMED IS:

1. A method of improving the amount of cetane in a fuel comprising the step of adding a  $\beta$ -carotene that was dissolved in an inert atmosphere to said fuel.
2. A method of making a cetane improver comprising:  
5 providing  $\beta$ -carotene that was dissolved in an inert atmosphere;  
providing an alkyl nitrate; and  
mixing the  $\beta$ -carotene with the alkyl nitrate.
3. The method of Claim 2, wherein the alkyl nitrate is 2-ethylhexyl nitrate.
4. The method of Claim 2, wherein the inert atmosphere is nitrogen.
- 10 5. The method of Claim 2, further comprising the step of mixing the  $\beta$ -carotene with toluene prior to mixing the  $\beta$ -carotene with the alkyl nitrate.
6. A cetane improver made by the method of Claim 2.
7. A cetane improver comprising a non-oxygenated  $\beta$ -carotene.
8. The cetane improver of Claim 7, further comprising an alkyl nitrate.
- 15 9. The cetane improver of Claim 7 or 8, further comprising a toluene.
10. The cetane improver of Claim 8 or 9, wherein the alkyl nitrate is 2-ethylhexyl nitrate.
11. A No. 2 diesel fuel comprising the cetane improver of Claim 7.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/40509

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10L 1/18, 1/22

US CL : 44/307,323

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/307,323

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST(beta aj carotene, diesel adj fuel, inert adj atomsphere, nitrate, ethylhexyl adj nitrate, carotene adj toluene)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,274,835 A (JORDAN) 23 June 1981, abstract col. 1, line 53 to col. 2, lines 1-6 and 12 to col. 3, lines 1-25 and claims 3 and 5.	1-11
Y	US 2,582,192 A (DENISON, JR.) 08 January 1952, col. 1, 27-37.	2-6 and 8-10
Y	US 4,208,190 A (MALEC) 17 June 1980, abstract, col. 2, lines 26-36 and 53.	2-6 and 8-10
Y	US 5,826,369 A (JORDAN) 27 October 1998, abstract, col. 2, line 61 to col. 3, lines 13 and claims 1-17.	1-11
Y,P	US 6,193,766 B1 (JORDAN) 27 February 2001, abstract, col. 3, lines 15-40 and claims 1-11.	2-6 and 8-10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

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# INTERNATIONAL SEARCH REPORT

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0,457,589 A1 (CUNNINGHAM et al) 21 November 1991, abstract, page 4, lines 5-55 and 35, and claims 1-10.	2-6 and 8-10